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ADP023764

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TITLE: Proceedings of the HPCMP Users Group Conference 2007. High Performance Computing Modernization Program: A Bridge to Future Defense held 18-21 June 2007 in Pittsburgh, Pennsylvania

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ADP023728 thru ADP023803

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Direct Quantum Mechanical Simulations of Shocked Energetic Materials Supporting Future Force Insensitive Munitions Requirements

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Abstract

Quantum mechanical calculations based on density functional theory (DFT) are used to study dynamic behavior of shocked polymeric nitrogen, a novel energetic material. We report results on system sizes in excess of 3,000 atoms. Such calculations on system sizes within the 1,000 atom range remain problematic using standard implementations of DFT. We evaluate the feasibility of using several available DFT codes for this work through comparison of scalability and resource requirements. In this study, we utilize a recently developed highly-scalable localized orbital DFT code, CP2K, designed to treat large systems. Scaling and performance benchmarks of the CP2K on several Department of Defense (DoD) high performance computing (HPC) computers are presented for a variety of system sizes and shapes. Additionally, we report preliminary calculations on the conventional explosive nitromethane. In those calculations in excess of 3,500, atoms are treated.

1. Introduction

The changing nature of international conflicts requires the transformation of war-fighting capabilities within the Department of Defense. The attainment of the transformation of the military force structure depends on the development of lighter-weight, more robust and integrated armor materials and for systems to meet the requirements for speed, mobility, and rapid deployment of weapon platforms and to enhance combat personnel effectiveness, and survivability in the face of a widening range of more lethal and countering threats. New energetic materials, with substantially enhanced performance and reduced vulnerabilities, must be developed for future weapons systems to meet these criteria. Advanced Energetic Materials (AEM) are required to enable high priority military missions ranging

from Hard and Deeply Buried Target Defeat, to Advanced Propulsion, to lightened highly mobile force evolution and the thrust towards miniaturized munitions and systems. It is recognized that weapons superiority is dependent on the development of AEM. The National Advanced Energetics Initiative recognizes that developments in computational chemistry and physics-based modeling using HPC are among areas that can provide the key factors that will enable breakthroughs in the performance of energetic materials. Our continued efforts focus on a fundamental understanding of the dynamic behavior of new and existing energetic materials (EMs) that can be used to design new or modify existing weaponry for optimal performance. In particular, we are interested in obtaining a first-principles description of the atomic-level details of shock initiation of AEMs. In prior years, atomic-level simulations of shocked materials have been limited to classical molecular dynamics (MD) treatments. While such simulations have been extremely useful in providing atomic-level detail into dynamic response of shocked materials, the classical models are not accurate or physically realistic over the wide range of thermodynamic conditions present under shock compression. On the other hand, the quantum mechanical approach of Density Functional Theory (DFT)^[1] has demonstrated accuracy over a wide range of temperatures and pressures and does not suffer the limitations of classical models^[2]. For this reason, we have chosen to apply DFT MD methods to the study of AEM to obtain the desired first-principles description of material response to shock initiation.

In our applications of DFT to AEM, we first apply these methods on a simple system as a proof of principle. We have chosen for our test system a polymorphic phase of nitrogen called cubic gauche nitrogen (cg-N)^[3]. While nitrogen seems far-removed from conventional EMs (which are typically large, polyatomic organic molecular

crystals), under pressure it has been shown to take on a polymeric form. The cg-N form is a bulk three dimensional covalent network like diamond, in which every atom has three neighbors compared to diatomic molecular forms of nitrogen. Since diatomic nitrogen has the strongest bond in nature, the amount of energy released from the polymeric form as it transitions to the more stable standard state is extremely large. The products of the conversion are very simple; the solid, which is composed of singly-bonded nitrogen, transitions to the diatomic triply-bonded gaseous form and small chains. The amount of energy available for release through complete conversion is several times that of RDX by weight and volume. Simulation has confirmed that cg-N is stable at low temperatures and pressures, but will react very rapidly and release large quantities of energy when sufficiently perturbed^[4]. The simplicity and reactivity of this single-element system make it an ideal physically realistic test case for simulation of shock initiation.

In this paper, we will describe our initial efforts to study the response of shocked cg-N using DFT. This paper will briefly describe the theoretical methods, the computational details, software explored to enable adequate treatment of the calculations, HPC resources used, and results of the calculations to date.

2. Level of Theory

DFT is not considered the most accurate quantum mechanics method available, but it has become a state-of-practice in the scientific community due to its computational efficiency relative to other, more accurate methods. For example, the CCSD(T)^[5] quantum chemistry techniques are formally $O(N^7)$ where N reflects the number of electrons in the system in sharp contrast to DFT methods which typically range from $O(N)$ – $O(N^3)$. In the DFT formalism each electron is treated independently and interacts with other electrons not directly but only through an effective potential which is a function of the total charge density. This mean-field approximation drastically reduces the computational effort compared to higher level quantum chemistry methods while maintaining accuracy sufficient for many applications. Advances in approximations, efficient mathematical algorithms, and implementations on scaleable platforms have further increased application of DFT to large and complex systems of interest to the DoD.

In this study, we have utilized the Perdew-Burke-Ernzerhof^[6] form of the Generalized Gradient Approximation of the DFT as implemented in the local orbital basis code CP2K. We have used the double-zeta valence polarization basis which corresponds to a total of thirteen basis functions per nitrogen atom. Total energies

and forces were converged to $1.6e-4$ and $2.6e-5$ a.u., respectively and were used throughout these calculations.

3. Computational Details

Two sets of simulations were performed. The first is a DFT MD simulation of a filament of material subjected to flyer-plate impact. This is a non-equilibrium molecular dynamics (NEMD) simulation in which the dynamic response of the material can be directly observed through monitoring the time progression of atomic positions and velocities. The second set also utilizes DFT-MD, except the simulations calculate properties of the material under thermodynamic equilibrium at various conditions. Equation-of-State (EOS) information is obtained from these simulations and used to generate the shock Hugoniot, a special set of points satisfying the conservation equations of mass, momentum and energy across the shock front between the quiescent crystal and its final shocked state. We will refer to this method as the Erpenbeck^[7] approach, named after an author who used classical MD to generate the shock Hugoniot of a simple model material.

A. Direction Shock Simulation

The simulation cell consists of a filament of energetic material composed of 2,304 atoms arranged in the equilibrium cg-N configuration at $T=250K$, $P=1$ atm. Periodic boundary conditions are imposed in the two directions perpendicular to the direction of shock propagation. In this study, the shock wave will initiate at one edge of the filament using a small segment of material in which each atom is assigned large initial velocities in the direction of shock impact. The remaining atoms in the filament are at a thermodynamic equilibrium ($T=250K$, $P=1$ atm). The resulting integration of the microcanonical equations of motion using DFT-MD for this set of initial conditions will simulate shock initiation through flyer-plate impact. The position of the shock discontinuity through the filament is monitored, and when it approaches the end of the filament, additional material is added at the end of the filament ahead of the progressing shock wave. The state of the material that is added is also in thermodynamic equilibrium and its atomic arrangements are consistent with that of cg-N at that thermodynamic state.

Since a shock wave travels faster than the sound speed of the material, there is no need to simulate large portions of undisturbed material ahead of the shock front; rather, we have found in earlier classical MD studies that adding material ahead of the propagating shock front is sufficient to adequately describe the dynamics of the process. This method has been used in many classical

MD simulations of shock waves^[8]. Obviously, in such a simulation scheme, the simulation size grows as the shock wave progresses through the material, significantly increasing the computational demands during the simulation.

B. Erpenbeck Method^[7]

The thermodynamic quantities of a material in the quiescent and final shocked states are related by the conservation equations of mass, momentum, and energy across the shock front and are represented by the shock Hugoniot, a set of EOS points that satisfy the Hugoniot function:

$$H_g(T, V) = 0 = E - E_0 - \frac{1}{2}(P + P_0)(V_0 - V) \quad (1)$$

In this equation, E , P , and V are the internal energy/unit mass, pressure, and volume/unit mass, respectively. E_0 , P_0 , and V_0 are the internal energy/unit mass, pressure and volume/unit mass in the quiescent state. The procedure for identifying points on the shock Hugoniot is straightforward. For each volume, a series of DFT-MD simulations of the Number of particles, Volume,

and Temperature (NVT) ensemble are performed over a range of temperatures. Once convergence of the thermodynamic properties is reached for each simulation, the Hugoniot function is evaluated. The resulting set of calculations will produce a series of $H_g(T)_V$, which is then fitted to a polynomial from which the Hugoniot temperature (T_{Hg}) can be identified from $H_g(T_{Hg})_V = 0$. Once this has been done, the dependence of either the pressure or the internal energy on temperature can be determined through fitting these quantities to polynomials and evaluating them at T_{Hg} . Each of the calculations used to construct the shock Hugoniot was composed of 256 atoms, with their initial arrangement consistent with that of the cg-N structure at $T=298K$, $P=1$ atm. Each trajectory was first equilibrated for 4,000 time-steps and thermodynamic values were averaged over the subsequent 4,000 time-steps (1 time-step=1 fs).

4. Suitability of Available Codes

For this Challenge Project, we evaluated six packages that implement DFT for solid state applications (Table 1).

Table 1. Evaluated DFT Packages^[9]

Package	Representation	Maximum Size (Atoms)	Scalability (Processors)	License
ABINIT	PW	100	8	Open Source
CP2K	LO	4,000+	512	Open Source
Espresso	PW	1,000	512	Open Source
PARATEC	PW	1,000	512	Limited
SIESTA	LO	1,000+	128	Commercial
Socorro	PW	1,000	512	Open Source
VASP	PW	500	128	Commercial

These differ mainly in how they represent the electrons and can be categorized into two main families: Planewaves (PW) and Localized Orbitals (LO). The PW method is a simple robust formalism with a long history. It is the “gold standard” in DFT calculations owing to its systematically improvable basis (sometimes referred to as PW accuracy). Its main drawback is the large number of PWs required to adequately describe the electronic space. Consequently, the number of atoms that can be studied with available implementations at this time is limited to ~1,000 due to the CPU and memory requirements associated with large numbers of PWs. The LO method generally offers excellent accuracy at a fraction of the computational cost of the PW approach, although it does

not have a systematically improvable basis. Table 1 provides a description of the scalability and applicability of various DFT codes on large systems of atoms and their availability. In our work, we are primarily interested in monitoring the temporal behavior for systems in the 1,000+ atom range. Therefore, PWs do not appear to be an option for use at this time for these large system sizes. Additionally, our primary calculations are NEMD of extreme energy-releasing events, and thus PW accuracy is not essential as errors in the trajectory integration will be on the same order as those of LOs. Therefore, the more appropriate DFT approach use in this work is the LO method. The results shown in Table 1 indicate that for

efficiency, scalability, and system size, CP2K is the most suitable software package for our use.

5. Results

A. DFT MD Simulations

Two types of MD calculations were performed to provide insight into the nature of shocked cg-N. The less computationally demanding is the generation of the shock Hugoniot using equilibrium MD methods. This methodology does not require large numbers of atoms and uses MD to generate the EOS for the materials. Its computational cost comes from the number of EOS points needed to map out the shock Hugoniot. Each point on the shock Hugoniot (Figure 1) was obtained by interpolating the Hugoniot function for four EOS points. In total this has required in excess of 500,000 CPU hours on the hpc11 (SGI Origin 3900).

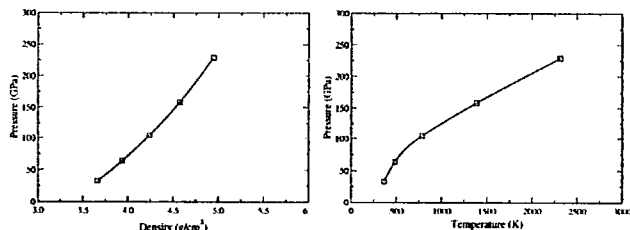


Figure 1. Principal shock Hugoniot of cg-N in pressure-density (left) and pressure-temperature (right) planes

As evident in Figure 1, no anomalous behavior was found in the principal shock Hugoniot. However, additional NVT simulations showed that cg-N will undergo a phase transition at approximately $P = 50$ GPa, $T = 4,000$ K; the material transitioned from the polymeric solid form to liquid composed of both atoms and molecules. The material in this state is not well characterized. Figure 2 shows three snapshots of the system at various time steps during the trajectory integration. The left-most frame shows the system in the initial cg-N arrangement, and the right-most frame shows a distribution of atoms and clusters ranging in size from two to ten atoms. The structure of the material is consistent with a liquid. The dynamic behavior of the material during this portion of the trajectory shows that the clusters are not stable as the atoms rapidly change partners. It is not known whether any true cluster formation is obtained. The middle frame is representative of a transient state of the material that appears to have some structure. Further calculations are needed in order to make a definitive characterization of the transient and final states of the material.

The more direct approach to characterizing a shocked material is a MD simulation of a shock wave propagating through a material. These calculations require orders of magnitude more computational resources than for those of the Erpenbeck-type calculations of the shock Hugoniot described heretofore due to requirements of a larger number of atoms and the rapidly changing electronic environment traveling with the shock wave. The upper pane of Figure 3 shows the left half initial filament used in the shock simulation. The filament is composed of 2,304 atoms in the equilibrium cg-N arrangement. The shock wave is initiated at the far left edge by assigning the 432 left-most atoms in the filament with an initial velocity in the direction of the shock propagation corresponding to 10 km/sec. The 108 right-most atoms in the filament are frozen during the dynamics simulation to preclude surface effects. As the shock wave progresses, quiescent material will be inserted immediately to the left of the frozen portion of the filament. In monitoring the dynamic behavior of the shocked material, we find that it appears to be a stiff material. By this, we mean that upon shock wave passage, the material does not maintain significant deformation and reverts to its near equilibrium configuration. We note that well after shock wave passage, the atoms at the left-most edge of the filament exhibit large vibrational amplitude motion and the material at this edge begins to decompose. The trajectory has not yet progressed to the point that we observe final product formation; however, formation of the molecular species appears to occur, as shown in the lower frame of Figure 3, which gives a snapshot of the shocked material 1.0 ps after flyer plate impact. The material that has decomposed from the filament appears to exist as either single atoms or hot di- or triatomics. Up to this point, the calculations of the direct shocked filaments using 128 processors on the John von Neumann cluster (JVN) have expended 1,000,000 CPU hours. Additionally 200,000 CPU hours were expended on hpc11 with up to 256 processors.

B. Scaling and Performance of CP2K

In this portion of the paper, we will describe the scaling and performance of the DFT code CP2K. "Fixed" denotes timings for a same-size problem across N processors. "Scaled" denotes timings for runs in which problem size is increased in direct proportion to number of processors. The left pane of Figure 4 shows fixed system size speedup for CP2K on various HPC systems for simulation cells of different shapes and sizes. Each simulation cell is composed of a series of unit cells replicated in the three Cartesian directions. Each unit cell is composed of 8 nitrogen atoms in the cg-N crystal structure. The shape and size of the simulation cell is

denoted by $\mathbf{h} \times \mathbf{k} \times \mathbf{l}$, where \mathbf{h} , \mathbf{k} and \mathbf{l} are integers. Sapphire (Cray T3E) produces the best fixed-size speedup with a large number of processes for near-cubic systems; JVN (Linux Network Cluster) exhibits much worse scaling behavior. However, for simulation cells that are extremely large in one dimension relative to the other two (such as those used in our shock wave simulations), JVN demonstrates greatly improved scaling. On JVN we see scaling of about 76% of ideal when doubling the number of processors for our simulations up to 256 processors, and less than 64 processes hits a memory swapping bottleneck. The right pane of Figure 4 shows the scaled speedup for DFT calculations using CP2K on various HPC platforms. DFT is an $\sim O(N^3)$ problem; thus, we expect the optimal scaled speedup to appear $\sim O(N^2)$. As is evident from the right pane of Figure 4, we see Jaws (Dell Woodcrest Cluster) outperforming other platforms. As in the fixed size timings, JVN is the worst performer. The relative performance between platforms is expected from the speeds and types of the processors. The relatively poor performance of JVN in both sets of these timings can be attributed somewhat to the age of the machine. Consequently, we expect the performance of the Army Research Laboratory's (ARL's) new MJM (Linux Network Woodcrest cluster) to exceed that of Jaws and the other systems.

6. Summary and Conclusions

The results that have been generated show no anomalous behavior and we project no unforeseen difficulties in achieving the scientific goals of this project.

We expect to conclude the cg-N shock calculations by the end of July 2007 and are currently designing the simulation cells that will be used in shock simulations of the conventional carbon-hydrogen-nitrogen-oxygen energetic material, nitromethane. At this time, we have simply relaxed a large simulation cell of nitromethane to establish the template that will be used to generate the filament that will ultimately be subjected to shock. This template is composed of 3,584 atoms arranged in the low-temperature, ambient pressure state. NVT-MD simulations of this system have used about 50K hours on JVN.

Acknowledgements

The DoD HPC Modernization Program supported this project by supplying supercomputer time under the Computing Challenge Project C2L. This computer time was made available at the DoD Major Shared Resources Centers (MSRCs) at the ARL MSRC and at the Aeronautical Systems Center MSRC.

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9. More information on these DFT codes can be found at their respective websites which are listed in the order which they appear in the Table : www.abinit.org, cp2k.berlios.de, www.pwscf.org, www.nersc.gov/projects/paratec, www.uam.es/departamentos/ciencias/fismateriac/siesta/, dft.sandia.gov/socorro/, and cms.mpi.univie.ac.at/vasp/.

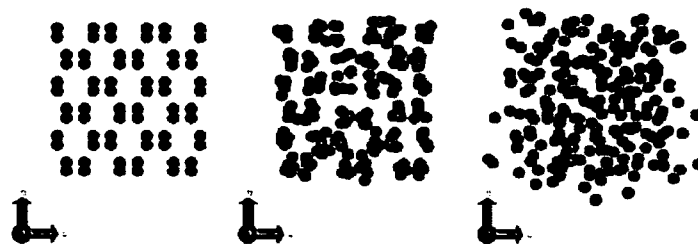


Figure 2. Snapshots of cg-N undergoing a phase transition at $t = 0$ (left-most frame), $t = 350$ fs (middle frame) and $t = 700$ fs (final frame) at $T = 4,000\text{K}$, $P = 50\text{GPa}$

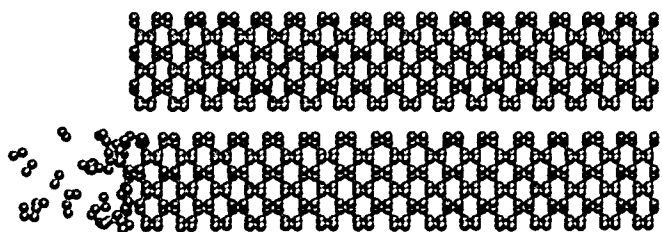


Figure 3. Snapshots of left half of the equilibrated crystal at the beginning of the shock simulation (upper) and at 1.0 ps after shock compression (lower)

